Synthesis, Crystal Structure and Fluorescent Properties of Silver and Cadmium Complexes (Postprint)

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Full Text

Preamble

Synthesis, Crystal Structure and Fluorescent Properties of Silver and Cadmium Complexes

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Abstract

Two novel complexes, [Ag(bix)]n·nNAA·nH2O (1) and [Cd(NAA)(phen)2(H2O)]2·2CH3COO ·H2O (2) (where bix = 1,4-bis(imidazol-1-ylmethyl)benzene, HNAA = -naphthylacetic acid, phen = 1,10-phenanthroline), have been successfully synthesized under hydrothermal conditions. Their structures were determined through elemental analyses, IR spectroscopy, thermogravimetric analysis, and single-crystal X-ray diffraction. Intermolecular hydrogen bonding and – stacking interactions extend these complexes into three-dimensional supramolecular architectures. Additionally, the luminescent properties of complex 2 were investigated in the solid state.

Keywords: hydrothermal synthesis; crystal structure; Ag(I) complex; Cd(II) complex; fluorescent properties

1. Introduction

Metallosupramolecular assemblies constructed from transition metals and organic bridging ligands have developed rapidly due to their intriguing structural diversity and potential applications as functional materials. However, the rational design of new materials for specific applications remains at an early evolutionary stage, with current research focusing primarily on understanding the factors that determine crystal packing. In recent years, several types of forces—including coordination bonding, hydrogen bonding, – stacking, and electrostatic interactions—have been effectively utilized to construct extended supramolecular networks. To date, coordination, hydrogen bonding, and – stacking interactions represent the most important driving forces in crystal engineering, and numerous networks assembled from mono- or polynuclear metal complexes via these interactions have been reported recently. The unique strength, directionality, and complementarity of such non-covalent interactions play key roles in constructing various architectures for molecular self-assembly and recognition.

Considering these aspects, we herein report the syntheses and crystal structures of two coordination supramolecules: [Ag(bix)]n · nNAA · nH2O (1) and [Cd(NAA)(phen)2(H2O)]2 · 2CH3COO · H2O (2). In the solid state, both complexes 1 and 2 form three-dimensional networks resulting from intermolecular hydrogen-bonding or – stacking interactions.

2. Experimental

2.1 Materials and Instruments

All chemicals for synthesis were commercially purchased and used without further purification. Elemental analyses of C, H, and N were performed on an Elementar Vario III Elemental Analyzer. IR spectra were recorded in the range of 4000–400 cm ^{1} on a Nicolet 6700 spectrometer using KBr pellets. Thermal stability (TG-DTA) studies were carried out on a Dupont thermal analyzer from room temperature to 800 °C. Powder X-ray diffraction (PXRD) patterns were collected in the 2 range of 5–50° with a scan speed of 0.1° · s ^{1} on a Bruker D8 Advance instrument using CuK radiation (= 1.54056 Å) at room temperature. Fluorescence studies were conducted on a computer-controlled JY Fluoro-Max-3 spectrometer at room temperature.

2.2 Synthesis

[Ag(bix)]n · nNAA · nH2O (1). Complex 1 was prepared by reacting Ag(OAc) with -naphthylacetic acid and 1,4-bis(imidazol-1-ylmethyl)benzene in an equimolar ratio in a mixture of CH3OH and H2O. A suitable amount of NaOH was added to adjust the pH to 7, and the solution was stirred at room temperature for 0.5 h until homogeneous. The mixture was then sealed in a 30 mL acid digestion bomb and heated at 140 °C for 5 days. After slow cooling to room temperature, colorless block crystals were obtained by filtration and dried in air. Yield: ~21% (based on Ag salt). Anal. Calcd. for C26H23AgN4O3: C, 57.05; H, 4.24; N, 10.24%. Found: C, 56.93; H, 4.05; N, 9.97%. IR (KBr pellet, cm ^{1}): 3385w, 3103w, 1565s, 1512w, 1379s, 1230w, 1074w, 792w, 710w, 650w, 539w.

[Cd(NAA)(phen)2(H2O)]2 · 2CH3COO · H2O (2). Complex 2 was prepared from a mixture of Cd(OAc)2 · 2H2O (0.026 g, 0.1 mmol), HNAA (0.019 g, 0.1 mmol), phen (0.04 g, 0.2 mmol), and H2O (18 mL) in a 30 mL Teflon-lined stainless steel vessel. The vessel was sealed and heated at 130 °C for 5 days. After cooling to room temperature at a rate of 5 °C/h, colorless block crystals of complex 2 were obtained. Yield: 27% (based on Cd salt). Anal. Calcd. (%) for C76H52Cd2N8O11: C, 61.76; H, 3.55; N, 7.58. Found (%): C, 61.08; H, 3.07; N, 7.01. IR (cm ^{1}): 3058w, 1584s, 1570w, 1378s, 1324w, 1144w, 848w, 722m, 632w.

2.3 X-ray Crystallography

All diffraction data for complexes 1 and 2 were collected on a Bruker/Siemens Smart Apex II CCD diffractometer with graphite-monochromated MoK radiation (= 0.71073 Å) at 293(2) K. Data reduction and absorption corrections were performed using SAINT and SADABS programs, respectively. The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares techniques using the SHELXL-97 crystallographic software package. All hydrogen atoms were generated geometrically and refined isotropically using the riding model.

For complex 1, a total of 4557 reflections were collected in the range 2.03 26.03°, of which 3601 were independent (Rint = 0.0194). The final R = 0.0455 and wR = 0.1137 for observed reflections with I > 2 (I), and R = 0.0587 and wR = 0.1217 for all data, with (Δ)max = 0.900 and (Δ)min = -0.802 e · Å ^{3}. For complex 2, a total of 12668 reflections were collected in the range 1.07 26.15°, of which 7090 were independent (Rint = 0.0710). The final R = 0.0551 and wR = 0.1112 for observed reflections with I > 2 (I), and R = 0.0950 and wR = 0.1220 for all data, with (Δ)max = 0.789 and (Δ)min = -0.396 e · Å ^{3}. Selected bond lengths and angles for complexes 1 and 2 are shown in Table 1 .

3. Results and Discussion

3.1 Structural Description

Single-crystal X-ray diffraction analysis reveals that complex 1 crystallizes in the P21/n space group and comprises a one-dimensional chain-like structure. The asymmetric unit contains one Ag(I) ion, one bix ligand, one HNAA ligand, and one crystal water molecule (Fig. 1 [Figure 1: see original paper]). Notably, the HNAA ligand does not coordinate to the Ag(I) ion but merely serves as a charge-balancing counterion. The Ag(1) ion is coordinated by two nitrogen atoms from two bix ligands (Ag(1)-N(1) = 2.127(3) Å, Ag(1)-N(4A) = 2.136(3) Å) with a coordination angle of 168.51(12)° around the silver center.

In the crystal structure of complex 1, the bix ligands adopt a trans-conformation bridging mode with a dihedral angle of 24.07° between the two imidazole rings, linking Ag(I) ions to form a one-dimensional zigzag chain with an Ag ··· Ag distance of 14.301 Å. The Ag(1) ion exhibits a slightly distorted linear coordination geometry. It is noteworthy that free -naphthylacetic acid and neighboring bix ligands contribute to chain formation through C-H ··· O and O-H ··· O hydrogen bonding interactions (Table 2). Additionally, a one-dimensional trapezoidal banded structure forms between adjacent chains and -naphthylacetic acid via C-H ··· O and O-H ··· O hydrogen bonds. Significant C-H ··· interactions exist between C(4) and the benzene ring C(5)-C(9) (symmetry code: 1-x, 1-y, -z), C(11) and benzene ring C(17)-C(22) (symmetry code: 1/2+x, 1/2-y, -1/2+z), C(13) and benzene ring C(21)-C(26) (symmetry code: 1/2+x, 1/2-y, -1/2+z), and C(24) and benzene ring C(5)-C(9) (symmetry code: 1/2+x, 1/2-y, 1/2+z) from symmetry-related bix and NAA ligands, with C-H ··· distances of 3.377(4), 3.829(5), 3.825(5), and 3.580(10) Å, respectively. Through these interactions, a two-dimensional layered structure is generated (Fig. 2 [Figure 2: see original paper]).

Single-crystal X-ray diffraction study reveals that complex 2 crystallizes in the monoclinic P21/n space group. The coordination environment of Cd(II) in 2 is shown in Fig. 3 [Figure 3: see original paper]. The crystal contains two coordination centers, Cd(1) and Cd(2), with identical coordination modes, along with four phen ligands, two HNAA ligands, two coordinated water molecules, one crystal water molecule, and two free acetate anions. The Cd(1) ion is six-coordinated by four nitrogen atoms from two different phen ligands (Cd(1)-N(1) = 2.429(4) Å, Cd(1)-N(2) = 2.371(4) Å, Cd(1)-N(3) = 2.381(4) Å, Cd(1)-N(4) = 2.385(4) Å), one carboxylate oxygen atom from the HNAA ligand (Cd(1)-O(1) = 2.183(4) Å), and one coordinated water molecule (Cd(1)-O(2W) = 2.291(3) Å), forming a distorted octahedral coordination geometry. The coordination angles around the cadmium center range from 69.07(15)° to 161.00(15)°. In this environment, one carboxylate oxygen atom (O(1)) and three nitrogen atoms (N(2), N(3), and N(4)) occupy the basal plane, while the remaining nitrogen atom (N(1)) and the coordinated water molecule (O(2W)) occupy axial positions from opposite directions. Notably, the acetate anion does not coordinate to the

Cd(II) ion and serves only as a charge-balancing counterion.

In the crystal structure of complex 2, phen ligands adopt a classic bidentate chelating mode, while HNAA ligands display a monodentate bridging coordination mode. In the structural unit, the upper and lower independent moieties are connected through O–H ⋯ O and C–H ⋯ O hydrogen bonding (Table 2) and – stacking interactions (Table 3) between pyridine rings of phen ligands and benzene rings of phen and NAA ligands. Each structural unit is further linked into a double-chain via O–H ⋯ O and C–H ⋯ O hydrogen bonding. Moreover, a two-dimensional layer architecture forms between these double-chains through O–H ⋯ O, C–H ⋯ O hydrogen bonding, and – stacking interactions, which are connected with free acetate anions to generate a three-dimensional supramolecular structure via O–H ⋯ O and C–H ⋯ O hydrogen bonding (Fig. 4 [Figure 4: see original paper]).

3.2 IR Analysis

The IR spectrum of complex 1 shows a broad absorption band at 3385 cm ^{1} corresponding to O–H stretching of crystal water molecules. Asymmetric and symmetric COO stretching modes of the lattice NAA anion are evidenced by very strong, slightly broadened bands at 1565 and 1379 cm ^{1}, consistent with the X-ray analysis results.

The IR spectrum of complex 2 shows a broad absorption band at 3058 cm ^{1} corresponding to O–H stretching of water molecules. Asymmetric and symmetric COO stretching modes of the lattice NAA anion are evidenced by very strong, slightly broadened bands at 1584 and 1378 cm ^{1}, which is also consistent with the X-ray analysis results.

3.3 Thermal Stability and Powder X-ray Diffraction

To confirm the phase purity of complexes 1 and 2, powder X-ray diffraction patterns were recorded and compared with simulated patterns calculated from single-crystal diffraction data (Fig. 5 [Figure 5: see original paper]), confirming the bulk samples are pure phases.

To better understand the thermal stability of complexes 1 and 2, their thermal decomposition behaviors were investigated from 50 to 800 °C under nitrogen atmosphere (Fig. 6 [Figure 6: see original paper]). The TG curve of 1 shows a weight loss of 3.10% from 50 to 70 °C, corresponding to loss of the crystal water molecule (calcd. 3.28%). The TG curve then shows a plateau, with framework decomposition beginning at 170 °C. The TG curve of 2 exhibits a weight loss of 10.00% from 50 to 252 °C, attributed to loss of water molecules and acetate anions (calcd. 10.65%). The TG curve shows a plateau, with framework decomposition commencing at 255 °C.

3.4 Photoluminescent Properties

The solid-state emission spectrum of complex 2 at room temperature is shown in Fig. 7 [Figure 7: see original paper]. Complex 2 exhibits blue photoluminescence with an emission maximum at approximately 465 nm upon excitation at 325 nm. To understand the nature of this emission, we first examined the photoluminescence properties of free HNAA ligand (em = 275 nm) and confirmed it emits no luminescence in the 400-800 nm range. We then investigated the emission spectrum of phen (em = 285 nm) itself, which also showed no luminescence in the 400-800 nm range, consistent with previous reports. Therefore, based on earlier literature, the emission band can be assigned to ligand-to-metal charge transfer (LMCT).

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Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for 1 and 2

Complex 1		Complex 2	
Distances		**Distances**	
Ag(1)-N(1)	2.127(3)	Cd(1)-O(1)	2.183(4)
Ag(1)-N(4A)	2.136(3)	Cd(1)-O(2W)	2.291(3)
		Cd(1)-N(1)	2.429(4)
Angles		Cd(1)-N(2)	2.371(4)
N(1)-Ag(1)-N(4A)	168.51(12)	Cd(1)-N(3)	2.381(4)
		Cd(1)-N(4)	2.385(4)
		Cd(2)-O(3)	2.190(4)
		Cd(2)-O(1W)	2.307(3)
		Cd(2)-N(5)	2.372(4)
		Cd(2)-N(6)	2.383(4)
		Cd(2)-N(7)	2.392(4)
		Cd(2)-N(8)	2.416(4)
		Angles	
		O(1)-Cd(1)-O(2W)	108.64(15)
		O(1)-Cd(1)-N(2)	102.61(16)
		O(2W)-Cd(1)-N(2)	89.16(14)
		O(1)-Cd(1)-N(3)	158.88(16)
		O(2W)-Cd(1)-N(3)	86.66(13)
		N(2)-Cd(1)-N(3)	91.80(14)
		O(1)-Cd(1)-N(4)	91.30(16)
		O(2W)-Cd(1)-N(4)	107.40(14)
		N(2)-Cd(1)-N(4)	153.87(14)
		N(3)-Cd(1)-N(4)	69.79(15)
		O(1)-Cd(1)-N(1)	85.69(15)
		O(2W)-Cd(1)-N(1)	156.42(14)
		N(2)-Cd(1)-N(1)	69.07(15)
		N(3)-Cd(1)-N(1)	85.16(13)
		N(4)-Cd(1)-N(1)	90.39(14)
		O(3)-Cd(2)-O(1W)	106.69(14)
		O(3)-Cd(2)-N(5)	93.10(15)
		O(1W)-Cd(2)-N(5)	108.01(13)
		O(3)-Cd(2)-N(8)	100.29(15)

Complex 1		Complex 2	
		O(1W)-Cd(2)-N(8)	87.29(13)
		N(5)-Cd(2)-N(8)	155.94(14)
		O(3)-Cd(2)-N(6)	161.00(15)
		O(1W)-Cd(2)-N(6)	87.12(13)
		N(5)-Cd(2)-N(6)	69.82(15)
		N(8)-Cd(2)-N(6)	93.21(14)
		O(3)-Cd(2)-N(7)	83.50(14)
		O(1W)-Cd(2)-N(7)	155.95(13)
		N(5)-Cd(2)-N(7)	92.77(14)
		N(8)-Cd(2)-N(7)	69.25(14)
		N(6)-Cd(2)-N(7)	88.92(14)

Symmetry transformations used to generate equivalent atoms: 1: A: x-1, y, z+1

Table 2. Hydrogen Bonds for Complexes 1 and 2

D-H ⋯ A	d(D-H) (Å)	d(H ⋯ A) (Å)	d(D ⋯ A) (Å)	(DHA) (°)	Symmetry Codes
O(1W)-H(1WA)⋯O(1)	0.85	2.03	2.881(5)	175	1+x, y, z
O(1W)-H(1WB)⋯O(2)	0.85	1.88	2.722(4)	171	1-x, -y, -z
C(2)-H(2) ⋯ O(1)	0.93	2.58	3.197(5)	124	-1/2+x, 1/2-y, 1/2+z
C(8)-H(8) ⋯ O(1)	0.93	2.58	3.387(5)	146	1/2+x, 1/2-y, 1/2+z
C(12)-H(12)⋯O(2)	0.93	2.52	3.140(5)	124	1/2+x, 1/2-y, -1/2+z
O(3W)-H(3WA)⋯O(6)	0.85	2.15	2.988(8)	169	1-x, -y, 1-z
O(3W)-H(3WB)⋯O(6)	0.85	2.47	3.303(8)	168	-1/2+x, 1/2-y, 1/2+z
C(5)-H(5) ⋯ O(8)	0.93	2.56	3.471(7)	168	1/2+x, 1/2-y, 1/2+z

D-H ⋯ A	d(D-H) (Å)	d(H ⋯ A) (Å)	d(D ⋯ A) (Å)	(DHA) (°)	Symmetry Codes
C(15)-H(15)⋯O(6)	0.93	2.38	3.205(9)	147	1-x, 1-y, 1-z
C(20)-H(20)⋯O(7)	0.93	2.45	3.240(9)	142	1/2-x, 1/2+y, 1/2-z
C(26)-H(26A)⋯O(7)	0.96	2.61	3.541(8)	166	1/2-x, -1/2+y, 1/2-z
C(44)-H(44)⋯O(8)	0.93	2.44	3.350(8)	166	1/2-x, -1/2+y, 1/2-z
C(50)-H(50)⋯O(8)	0.93	2.46	3.377(8)	169	1/2-x, 1/2+y, 1/2-z
C(65)-H(65)⋯O(5)	0.93	2.29	3.192(12)	165	1-x, -y, -z

Table 3. Parameters between the Planes in 2

Plane I → Plane J	Distance between Ring Centroids (Å)	Dihedral Angle (°)	Perpendicular Distance of Plane I on Ring J (Å)	Perpendicular Distance of Plane J on Ring I (Å)
N(2)C(10)C(9)C(8)C(7)C(11) → C(31)C(32)C(33)C(34)C(35)C(36)i	3.652(5)	2.5(4)	3.567(2)	-3.570(4)
N(4)C(22)C(21)C(20)C(19)C(23) → N(5)C(37)C(38)C(39)C(40)C(48)	3.729(3)	1.0(2)	3.476(2)	3.492(2)
N(4)C(22)C(21)C(20)C(19)C(23) → C(40)C(41)C(42)C(43)C(47)C(48)	3.621(3)	2.1(2)	-3.471(2)	3.446(2)
C(4)C(5)C(6)C(7)C(11)C(12) → C(27)C(28)C(29)C(30)C(31)C(36)i	3.699(5)	4.1(3)	3.497(2)	-3.584(3)
C(4)C(5)C(6)C(7)C(11)C(12) → C(31)C(32)C(33)C(34)C(35)C(36)i	3.653(5)	3.4(4)	3.514(2)	-3.582(4)
C(16)C(17)C(18)C(19)C(23)C(24) → N(5)C(37)C(38)C(39)C(40)C(48)	3.636(3)	1.5(2)	-3.450(2)	3.476(2)

Plane I → Plane J	Distance between Ring Centroids (Å)	Dihedral Angle (°)	Perpendicular Distance of Plane I on Ring J (Å)	Perpendicular Distance of Plane J on Ring I (Å)
N(8)C(49)C(50)C(51)C(52)C(60) → C(67)C(68)C(69)C(70)C(71)C(72)ii	3.913(4)	5.7(3)	-3.685(2)	3.585(3)
C(52)C(53)C(54)C(55)C(59)C(60) → C(67)C(68)C(69)C(70)C(71)C(72)ii	3.806(5)	4.9(3)	-3.472(2)	3.590(3)

Symmetry codes: i = -x, -1-y, -z; ii = 1-x, 1-y, -z

Figure Captions

Fig. 1. View of the asymmetric unit of complex 1. All hydrogen atoms are omitted for clarity.
Fig. 2. View of the two-dimensional layered structure formed by C–H··· interactions in complex 1.
Fig. 3. View of the asymmetric unit of complex 2. All hydrogen atoms are omitted for clarity.
Fig. 4. View of the 3D supramolecular structure of complex 2.
Fig. 5. PXRD analysis of complex 1: bottom—simulated, top—experimental.
Fig. 6. TG curves of complexes 1 and 2.
Fig. 7. Solid-state emission spectrum of complex 2 at room temperature.

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